ON THE INFRARED SPECTRA OF MESITYLENE IN THE VAPOUR AND LIQUID STATES AND IN SOLUTIONS*

S B BANERJEE and K. C. MEDHI

Optics Department, Indian Association for the Cultivation of Science, Calcutta-32

(*Received, December* 19, 1959)

ABSTRACT. The infrared absorption spectra of mesitylene in the vapour and liquid states and in solutions in different solvents have been investigated with a Perkin-Elmer Model 21 spectrophotometer and some of the assignments of the observed frequencies of the molecule made by previous workers have been critically examined. It has been observed that the frequencies due to a mode of aromatic CH vibration and the CH vibration in the methyl group are affected with the change from the vapour to liquid state These frequencies are further affected in different ways when the compound is dissolved in different solvents. Attempts have been made to interpret these results

INTRODUCTION

It was observed in some recent investigations that the 0–0 electronic transition is forbidden in the spectrum of mesitylene in the vapour state (Sponer and Stallcup, 1948), but this transition becomes allowed in the case of the liquid (Sen, 1959) and its solutions in some solvents (Roy, 1957) This was explained by the latter workers by assuming that the three-fold symmetry of the molecule is disturbed due to association of the molecules in the liquid state and in solutions Information of such molecular association may be obtained from a comparative study of the infrared spectra of the substance in the vapour and liquid states and in solutions Pitzer and Scott (1943) reported an analysis of the infrared spectrum of mesitylene, based on the data reported by previous workers These data relate to the spectrum of the liquid or its solutions and it appears that no data are available for the vapour. Pitzer and Scott (1943) did not make any definite assignments of the vibrational frequencies of the molecule in the 3000 cm^{-1} region because of lack of suitable experimental data It would be expected that in analysing these and other frequencies the study of infrared spectrum of mesitylene in the vapour state would be helpful. With these objects in view an investigation of the infrared spectra of mesitylene in the liquid and vapour states and in solutions in different solvents was undertaken and the results have been discussed in the present paper

* Read in the symposium on Raman and Infrared Spectra held at Nainital in October 1959.

EXPERIMENTAL

Pure samples of mesitylene and of the solvents chloroform and carbon tetrachloride obtained from B.D.H. were used after being distilled under reduced pressure. The infrared spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. The absorption cell used for studying the spectrum of the vapour consisted of a pyrex tube 10 cm long and connected through a side tube to a small bulb containing the liquid. Two plane parallel sodium chloride plates at the two ends of the tube, held in position with the help of suitable gaskets and screws, served as the windows. A similar evacuated tube was placed in the path of the reference beam. Absorption cells of different thicknesses varying from .025 mm. to 0.1 mm. were used for studying the spectra of the solutions and a much thinner film was used in the case of the pure liquid. Suitable compensation cells were put in the reference beam to eliminate the bands due to the solvents in the case of the solutions. The calibration of the spectrophotometer was checked by noting the position of the CO_2 band.

RESULTS AND DISCUSSION

The infrared absorption curves are reproduced in Figs. 1, 2, 3 and 4 and the frequencies of the observed bands are given in Table I.

TABLE I
Infrared spectrum of mesitylene

Vapour	Liquid	5% Solution in $CHCl_3$	5% Solution in CCl_4
682 (s)	682	685	683
832 (vs)	835	836	835
925 (w)	925	915	920
1040 (ms)	1038	1038	1035
1238 (vw)	1200 (?)	1210	1230 (?)
1378 (ms)	1378	1378	1378
1440 (ms)	1442	1440	1460
1460 (s)	1470	1470	1472
1612 (vs)	1610	1605	1610
2882 (s)	2860	2858	2870
2950 (s)	2918	2918	2930
3050 (s)	3025	3005	3035

(a) *Assignment of the observed frequencies* :

It can be seen from Figs. 1(a) and 1(b) that in the vapour state mesitylene exhibits several bands which correspond to fundamental modes of vibration in the benzene ring as well as vibrations in the methyl group and that the spectrum shows two bands of moderate intensities at 3050 and 2950 cm^{-1} and a weaker band at 2882 cm^{-1}. Of these, the band at 3050 cm^{-1} is expected to be due to a CH vibration in the ring and the other bands to vibrations in the methyl group according to Pitzer and Scott (1943) who did not assign the band at 3050 cm^{-1} to any particular mode and also proposed that both the symme-

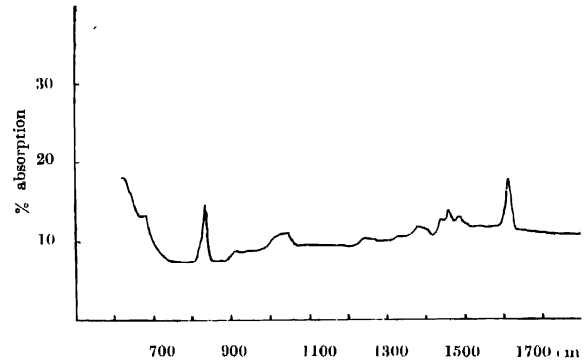


Fig. 1(a) Infrared spectrum of mesitylene (vapour at 26°C).

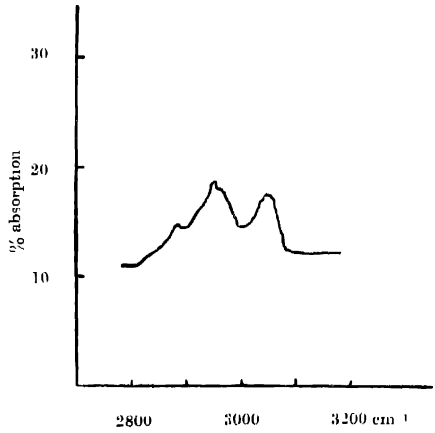


Fig 1(b) Infrared spectrum of mesitylene (vapour at 26°C).

Fig. 2(a) Infrared spectrum of mesitylene (liquid at 26°C)

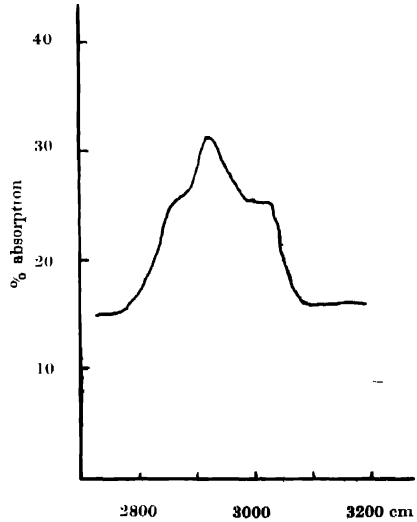


Fig. 2(b) Infrared spectrum of mesitylene (liquid at 26°C)

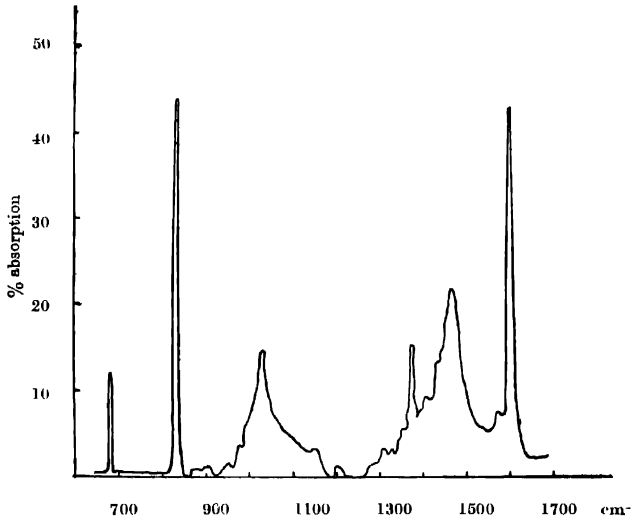


Fig. 3(a) Infrared spectrum of 5% solution of mesitylene in chloroform.

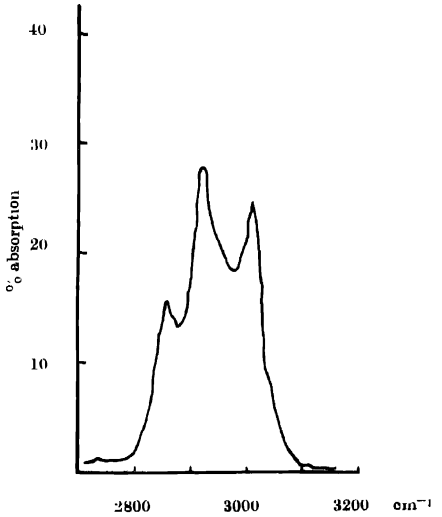


Fig. 3(b) Infrared spectrum of 5% solution of mesitylene in chloroform.

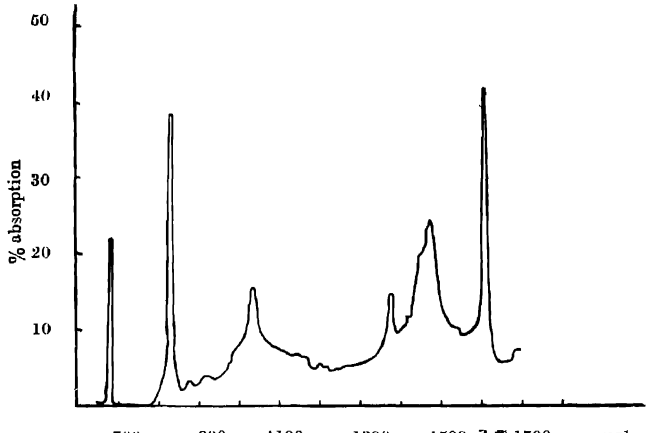


Fig. 4(a) Infrared spectrum of 5% solution of mesitylene in CCl_4

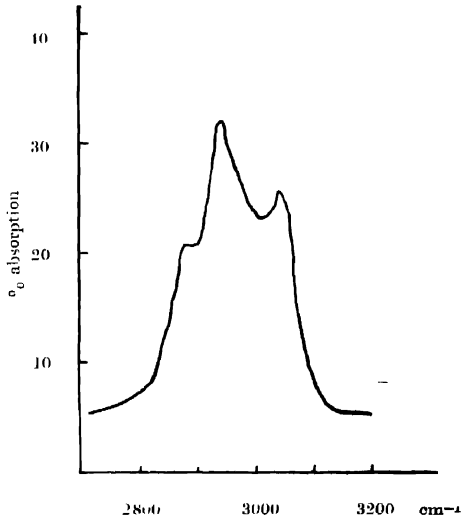
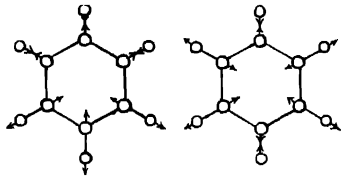


Fig. 4(b) Infrared spectrum of 5% solution of mesitylene in CCl_4.

tric and the asymmetric CH vibration in the methyl group would have the same frequency 2950 cm^{-1}. But from a review of the general trend of vibrational frequencies of the methyl group (Sheppard and Simpson, 1953) it appears that it would be proper to assign the band at 2950 cm^{-1} to asymmetric CH stretching vibration and that at 2882 cm^{-1} to the symmetric CH stretching vibration in the methyl group.



(*a*). (*b*)

Fig. 5.

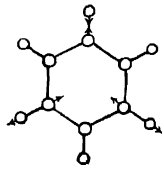


Fig. 6.

The large intensity of the band at 3050 cm^{-1}, which is expected to correspond to a mode of CH oscillation of the ring, points to the fact that it cannot be due to any mode of symmetric vibration. In assigning this band to an asymmetric mode of CH stretching vibration, the assignment of the bands in the infrared spectrum of 1,3,5-trideuterobenzene by Bailey *et al* (1946) has been followed They have shown that the doubly degenerate e_{2g} and e_{2u} modes in benzene of frequencies 3047 and 3080 cm^{-1} shown in Figs. 5(a) and 5(b) respectively, interact with double decomposition into a nearly pure doubly degenerate stretching vibration of deuterium atom only and another almost pure doubly degenerate vibration of hydrogen atom only. In the present case of 1,3,5-trimethylbenzene similar argument would lead us to expect an almost pure CH vibration and another almost pure C–CH_3 vibration as shown in figure 6. In that case the band at 3050 cm^{-1} would represent a CH vibration of symmetry class e' (Baily *et al.*, 1946) and this band would be allowed in the infrared thus accounting for its observed intensity in the infrared spectrum. There is a weak band at 1238 cm^{-1} in the spectrum of the vapour, which might represent the corresponding C–CH_3 vibration also of e'-class

On the long wavelength side there are several bands due to fundamental vibrations which include CH deformation vibrations within the methyl group. It is known from studies of infrared spectra of methylated compounds (Sheppard and Simpson, 1953) that in the methyl group there may be a symmetric deformation oscillation of frequency below 1400 cm^{-1} and two approximately doubly degenerate asymmetric modes of frequency near about 1450 cm^{-1}. Thus, it would be appropriate to attribute the band at 1378 cm^{-1} to the symmetric CH_3 bending, and the bands at 1440 and 1470 cm^{-1} to the two modes of asymmetric bending as done by Pitzer and Scott (1943) In addition to these there is a band

at 1040 cm^{-1} corresponding to wagging of the CH_3 group (Pitzer and Scott, 1943; Sheppard *et al.*, 1953).

The other molecular frequencies may be assigned to different modes by following Bailey *et al* (1946) who analysed the spectrum of 1,3,5-trideuterobenzene. Pitzer and Scott (1943) also have analysed these bands Thus the band at 682 cm^{-1} may be attributed to a C–C deformation perpendicular to the plane of the molecule (a_2''), that at 835 cm^{-1} to an out of plane hydrogen deformation (e') and the band at 1610 cm^{-1} to a mode of C–C stretching vibration (e')

(b) *Changes observed in the spectrum with the change from the vapour to liquid state and in solutions* :

As discussed above, in the spectrum of mesitylene vapour there is a band at 3050 cm^{-1} representing a CH stretching vibration in the benzene ring and two other bands at 2950 and 2882 cm^{-1} which represent respectively the asymmetric CH stretching vibrations in the methyl group When the vapour is liquefied these bands are found to shift to 3025, 2918 and 2860 cm^{-1} respectively, while the positions of the other bands except that at 1238 cm^{-1} remain unchanged. In the case of the solution in chloroform the band at 3050 cm^{-1} is further shifted to 3005 cm^{-1} When the substance is dissolved in the non-polar solvent carbon tetrachloride the three bands shift respectively to 2870, 2930 and 3035 cm^{-1} and the shifts are much smaller than those observed in the case of solution in chloroform The presence of a permanent electric moment in the chloroform molecule is thus responsible for the large change in the frequencies.

The weak band at 1238 cm^{-1} which has already been assigned to a $C\text{-}CH_3$ vibrational mode in the vapour state is absent in the spectrum due to a thin film of the liquid. However, when a thicker film, of thickness of the order of ·025 mm., is used a very weak band at 1200 cm^{-1} is just perceptible. Also, in the case of solutions of chloroform and carbon tetrachloride a weak band at 1210 cm^{-1} and 1230 cm^{-1} respectively is observed, which may correspond to this mode of vibration If the assignments of these bands due to the liquid and the solutions be correct then the $C\text{-}CH_3$ vibrational frequency also appears to be affected by change of state and environment In this case also the change observed in the case of the solution in CCl_4 is small

The shifts in the frequencies of the CH stretching vibration in the benzene ring and the CH stretching vibrations in the methyl group may indicate an association of the molecules in the liquid state through a virtual bond in which both the H-atoms of the ring and the CH_3 groups are involved. The changes in the intensity and frequency of the $C\text{–}CH_3$ vibration discussed above also support this conclusion. It is, however, unlikely that two CH_3 groups of neighbouring molecules form associated bonds to suppress the $C\text{–}CH_3$ vibration Therefore we have to postulate that such association is due to the influence of

π-electrons of the neighbouring molecules on the hydrogen atoms of the CH_3 group. This is also in conformity with the fact that the symmetry of the π-electron is disturbed and the 0–0 band appears in the ultraviolet absorption spectrum of the compound when the vapour is liquefied (Sen 1959). That only the aromatic CH oscillation frequency is further affected in the case of the solution in chloroform shows that the chlorine atom is involved in an association only with the H-atom of the ring and not with the CH_3 group

ACKNOWLEDGMENT

The authors are indebted to Professor S. C. Sirkar, D.Sc., F.N.I., for his kind interest and helpful discussion.

REFERENCES

Bailey, C. R., Hale, J. B., Herzfeld, N., Ingold, C. K., Leckie, A. H. and Poole, H. G., 1946, *J. Chem. Soc.*, 255.

Pitzer, K. S. and Scott, D. W., 1943, *J. Am. Chem. Soc.*, **65**, 803.

Roy, S. B., 1957, *Ind. J. Phys.*, **31**, 588.

Sen, S. K., 1959, *Ind. J. Phys.*, **33**, 41.

Sheppard, N. and Simpson, D. M., 1953, *Quart. Revs.*, **7**, 19

Sponer, H. and Stallcup, M. J., 1958, Contribution a l'Etude de la Structure Moleculaire, Victor Henri Memorial volume. (Desoer, lege), p. 222.